

10-  
86-

**This Page Is Inserted by IFW Operations  
and is not a part of the Official Record**

## **BEST AVAILABLE IMAGES**

**Defective images within this document are accurate representations of  
the original documents submitted by the applicant.**

**Defects in the images may include (but are not limited to):**

- **BLACK BORDERS**
- **TEXT CUT OFF AT TOP, BOTTOM OR SIDES**
- **FADED TEXT**
- **ILLEGIBLE TEXT**
- **SKEWED/SLANTED IMAGES**
- **COLORED PHOTOS**
- **BLACK OR VERY BLACK AND WHITE DARK PHOTOS**
- **GRAY SCALE DOCUMENTS**

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

0 279 374  
A1

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 88102079.6

(51) Int. Cl.4: B01J 23/88 , C07C 51/25 ,  
C07C 57/04 , C07C 45/32 ,  
B01J 35/10 , B01J 37/02

(22) Date of filing: 12.02.88

A request for correction of page 7 of the originally filed application documents has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 2.2).

(30) Priority: 17.02.87 JP 32354/87  
18.06.87 JP 150112/87

(43) Date of publication of application:  
24.08.88 Bulletin 88/34

(84) Designated Contracting States:  
BE DE ES FR GB IT

(71) Applicant: Nippon Shokubai Kagaku Kogyo Co., Ltd  
1, 5-chome, Koralbashi Higashi-ku  
Osaka-shi Osaka-fu 541(JP)

(72) Inventor: Kawajiri, Tasuya  
931-11, Hamada Aboshi-ku  
Himeji-shi Hyogo-ken(JP)  
Inventor: Uchida, Shinichi  
2-103, Noda 2-2, Jyoto-cho  
Himeji-shi Hyogo-ken(JP)  
Inventor: Wada, Masahiro  
3-23, Matsugaoka-cho  
Nishinomiya-shi Hyogo-ken(JP)  
Inventor: Onodera, Hideo  
931-11, Hamada Aboshiku  
Himeji-shi Hyogo-ken(JP)  
Inventor: Aoki, Yukio  
336-8, Tobo Taishi-cho  
Ibo-gun Hyogo-ken(JP)

(74) Representative: Kraus, Walter, Dr. et al  
Patentanwälte Kraus, Welsert & Partner  
Thomas-Wimmer-Ring 15  
D-8000 München 22(DE)

(54) Catalyst for oxidation of olefin or tertiary alcohol and process for production thereof.

(57) A catalyst used for producing, by catalytic gas phase oxidation of a C<sub>3</sub>-C<sub>8</sub> olefin or tertiary alcohol, the corresponding unsaturated aldehyde and unsaturated carboxylic acid, said catalyst characterized by comprising molybdenum, iron and bismuth and having a specific surface area in the range from 1 to 20m<sup>2</sup>/gr, a pore volume in the range from 0.1 to 1.0 cc/gr and a pore diameter distribution in which the pore diameters are collectively distributed in the range of each of from 1 to 10 microns and from 0.1 to 1 (exclusive) micron; and a process for preparing said catalyst by charging an unfired material powder into a centrifugal flow coating device to form particles having the average particle diameter of 2 to 10mm and then firing the particles.

EP 0 279 374 A1

This invention relates to an oxide catalyst comprising molybdenum, iron and bismuth and being suitable for producing, from an olefin or tertiary alcohol, the corresponding unsaturated aldehyde and unsaturated carboxylic acid and a process for the production thereof. More specifically, this invention relates to a catalyst which exhibits high activity and excellent durability owing to its specific properties and which is used for the oxidation of an olefin or tertiary alcohol and a process for the production of said catalyst with good reproducibility.

There are proposals for various catalysts for producing, from an olefin or tertiary alcohol (especially tertiary butanol), the corresponding unsaturated aldehyde (and unsaturated carboxylic acid) at high yields by a catalytic gas phase oxidation reaction. These proposals are mainly concerned with selection of components for catalysts and ratios thereof, and some of them are also concerned with selection of catalyst properties and production processes with reproducibility. For example, there are not a few proposals concerning catalyst properties such as specific surface area, pore volume, pore diameter, etc., with regard to catalysts used for the oxidation and ammoxxydation reactions of an olefin and comprising molybdenum, bismuth and iron. However, none of these proposed catalysts are on a satisfactory level, as will be mentioned hereinbelow.

With regard to the specific surface area, catalysts having specific surface areas in the range from 0.01 to 50 m<sup>2</sup>/g are described in Japanese Patent Publications Nos. 21081/1972, 10434/1977, 13488/1969, 5632/1978, 36384/1980, 24658/1981, 28180/1981 and 29139/1983 and Japanese Laid-Open Patent Publication No. 26690/1973. However, these catalysts are not satisfactory as industrial catalysts, since they have low activity in spite of defined high reaction temperatures or they have low selectivity to a corresponding unsaturated aldehyde. With regard to the pore volume, Japanese Laid-Open Patent Publication No. 119837/1982 describes that the pore volume of 0.2 to 0.4 cc/g is preferable. However, Examples thereof merely disclose the use mainly in ammoxxydation. With regard to the pore diameter, the same Japanese Laid-Open Patent Publication No. 119837/1982 describes that the average pore radius of not less than 2,000Å is preferable. The pore radii therein are controlled by addition of organic substance such as cellulose, etc., to material for catalyst. Japanese Patent Publication No. 113141/1983 describes, with regard to the pore diameter, that the pores having a diameter smaller than 100Å should be less than 3%. However, the catalysts disclosed therein all have low activity, and none of them can be used as an industrial catalyst for producing acrolein and acrylic acid or methacrolein and methacrylic acid at high yields by oxidation of propylene, isobutylene or tertiary butanol.

In the case of producing acrolein and acrylic acid or methacrolein and methacrylic acid by an oxidation reaction of propylene, isobutylene or tertiary butanol by the use of a reaction apparatus having a fixed bed or moving bed, catalysts are used, in general, in the form of pellets having a suitable size. Such pellets are formed by using a tablet-forming machine, extruder, pill-forming machine, rolling particile-forming machine, etc. However, there are many cases where it is difficult to form pellets without degradation of catalyst performance, and most cases show poor reproducibility of catalyst performance.

Therefore, the present inventors made an assiduous study of those causes of variations of catalyst performance which take place at the time of preparing catalyst pellets. As a result, they have found that, in catalysts containing Mo, Fe and Bi as essential components, the catalyst performance decreases to a great extent and the performance and physical property values vary depending upon the methods of formation thereof. The main cause thereof is that the forming procedure has influence on the pores of a catalyst and has consequent influence on the specific surface area, pore volume and average pore diameter of the catalyst.

As a result of the present inventors' further study, they have found that a catalyst containing Mo, Fe and Bi as essential components has to meet three conditions, in order to exhibit excellent properties, that it has a specific surface area in the range from 1 to 20m<sup>2</sup>/gr, that it has a pore volume in the range from 0.1 to 1.0 cc/gr and that it has a pore diameter distribution in which its pore diameters are collectively distributed in the range of each of from 1 to 10μm and from 0.1 to 1 (exclusive)μm.

Accordingly, the present invention provides a catalyst which comprises containing Mo, Fe and Bi and having the above three properties in combination and which is used for producing, by catalytic gas phase oxidation of a C<sub>3</sub>-C<sub>5</sub> olefin or tertiary alcohol, the corresponding unsaturated aldehyde and unsaturated carboxylic acid.

In the present invention, the well-balanced presence of pores having pore diameters of 1 to 10μm and pores having pore diameters of 0.1 to 1 (exclusive)μm is one of the important conditions. Catalysts for an oxidation reaction of propylene exhibit performance enhanced in both catalyst activity and selectivity when the catalysts have a pore diameter distribution in which the pore volume consisting of pores having pore diameters in the range from 0.1 to 1 (exclusive)μm is not less than 30%, preferably in the range from 45 to 80%, based on the entire pore volume and the pore volume consisting of pores having pore diameters in

the range from 1 to 10 $\mu$ m is not less than 20%, preferably in the range from 25 to 60%, based on the entire pore volume. On the other hand, it is one of the important conditions for the performance of catalysts used for an oxidation reaction of isobutylene or tertiary butanol that the ratio of the pore volume consisting of pores having pore diameters in the range from 1 to 10 $\mu$ m should be greater than the ratio of the pore volume consisting of pores having pore diameters in the range from 0.1 to 1 (exclusive) $\mu$ m.

In general, a pore having a smaller pore diameter has a larger contribution toward the surface area and pore volume. However, in the catalyst comprising Mo, Fe and Bi for oxidation of an olefin or tertiary alcohol in the present invention, the mere larger ratio of the smaller pores [i.e., pores having pore diameters in the range of 0.1 to 1 (exclusive) $\mu$ m] is not sufficient to obtain the aforementioned activity and selectivity, and the fairly larger ratio of the larger pores (i.e., pores having core diameters in the range of 1 to 10 $\mu$ m) is necessary as well.

By forming an unfired catalyst material powder into pellets having the average diameter of 2 to 10mm by the use of a centrifugal flow coating device, the catalyst having the above physical properties in the present invention can be obtained with very good reproducibility as compared with usual formation methods. In usual formation methods of catalysts, a rolling particle-forming method, marmerizer forming method, fluidized bed particle-forming method, etc., are used for the preparation of spherical shapes, and an extrusion method, tablet-forming method, etc., are used for cylindrical shapes. However, in the case of using these formation methods, it is difficult in many cases to form catalysts without degrading the catalyst performance, the performance varies widely and the reproducibility is often poor. In contrast thereto, in the present invention, the use of a centrifugal flow coating device, which is simple and good in producibility, makes it possible to prepare spherical or particulate catalysts having the aforespecified specific surface area, pore volume and pore diameter distribution, with good reproducibility. Further, the formation by a centrifugal flow coating device has advantages that catalysts having a narrow distribution of particle size can be obtained and that, since said catalysts are particulate or spherical, the catalysts have high mechanical strength, little pressure loss and high resistance to wear and are easy to fill in or take out from a reaction apparatus.

A centrifugal flow coating device and the use thereof are known as one method of forming powder material into particles. For example, Japanese Patent Publication No. 10878/1971 discloses them as a method of forming sugar coatings of medicaments, and Japanese Patent Publication No. 17292/1977 discloses the coating of particulate cores with a catalyst or carrier by a centrifugal flow coating device.

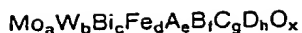
The present invention applies this method to the preparation of an oxide catalyst comprising Mo, Fe and Bi elements as essential components, and easily makes it possible to obtain a spherical or particulate catalyst having the aforespecified specific surface area, pore volume and pore diameter distribution and having high physical strength, by only using, as a binder, a liquid such as water, or by optionally using, in combination therewith, a substance which gives pores into a catalyst by combustion or volatility at the time of firing.

As a preparation example by a centrifugal flow coating device, there can be cited a method which comprises charging a powder of an unfired oxide composition not shaped or pre-stage catalyst particle material composition not converted to oxide into a centrifugal flow coating device, forming the powder into particles with blowing heated air thereinto and spraying a binder such as water, taking out the particles grown to the desired size in batch-type operation or in successive operation, then drying the particles as necessary and thereafter firing them.

The catalyst of the present invention can be used by diluting it with an inert carrier or by holding it on an inert carrier according to a case where it is necessary. In the formation of particles, it is preferable to use, as a core, granules obtained by preforming a powder of catalyst per se to a size about 10 times as large as that of the material powder. Naturally, an inert carrier can be also used as this core. Examples of the inert carrier include silicon carbide, silica, alpha-alumina and others known as a refractory material. With regard to a catalyst powder for coating to grow a particle diameter, it is preferable to preadjust it to not more than 100 mesh.

In order to produce a catalyst having the specific surface area, pore volume and pore diameter distribution specified by the present invention with good reproducibility, it is possible to add, for example, a polyvinyl alcohol, stearic acid, etc., to a material particles at the time of preparation of a catalyst powder or add it to a catalyst powder at the time of shaping. In the case, for example, when it is necessary to make the degree of powdering smaller, it is possible to use a whisker or glass fiber. As a binder of the powder, it is also possible to use water, cellulose, ammonium nitrate, graphite, starch, etc. Organic solvents such as alcohol, acetone, etc., can be used as well.

The catalyst of the present invention comprises Mo, Fe and Bi as essential components. Most preferably, it has a composition represented by the following formula.



wherein Mo denotes molybdenum, W denotes tungsten, Bi denotes bismuth, Fe denotes iron, A denotes at least one element selected from the group consisting of nickel and cobalt, B denotes at least one element selected from the group consisting of alkali metal, alkali earth metal and thallium, C denotes at least one element selected from the group consisting of phosphorus, tellurium, antimony, tin, cerium, lead, niobium, boron, arsenic, manganese and zinc, D denotes at least one element selected from the group consisting of silicon, aluminum, titanium and zirconium, and O denotes oxygen; and further, a, b, c, d, e, f, g, h and x denote atomic ratios respectively, when the olefin is propylene and when  $a = 2$  to 10,  $b = 0$  to 10 and  $a + b = 12$ , then  $c = 0.1$  to 10,  $d = 0.1$  to 10.0,  $e = 2$  to 20,  $f = 0.005$  to 3.0,  $g = 0$  to 4.0,  $h = 0.5$  to 15 and x is a numerical value determined depending upon the atomic values of the other elements than oxygen, and when the olefin is isobutylene or when the tertiary alcohol is tertiary butanol and when  $a = 12$ , then  $b = 0$  to 10,  $c = 0.1$  to 10,  $d = 0.1$  to 20,  $e = 2$  to 20,  $f = 0$  to 10,  $g = 0$  to 4,  $h = 0$  to 30 and x is a numerical value determined depending upon the atomic values of the other elements than oxygen.

A catalytic gas phase oxidation using a catalyst of the present invention is carried out by introducing a mixture gas consisting of 1.0 to 10% by volume of an olefin or tertiary butanol, 3 to 20% by volume of molecular oxygen, 0 to 60% by volume of water vapor and 20 to 80% by volume of an inert gas such as nitrogen, carbon dioxide gas, etc., onto the catalyst at a temperature in the range from 250 to 450°C, at a pressure of an atmospheric pressure to 10 atm and at a space velocity of 300 to 7,000 hr<sup>-1</sup> (STP).

The following Examples and Comparative Examples will illustrate the present invention more in detail, however, the present invention is not limited thereto. In the present specification, the conversion, selectivity and total yield in a single flow are respectively defined as follows.

Conversion ratio (mol%) =

$$\frac{\text{Number of moles of reacted propylene, isobutylene or tertiary butanol}}{\text{Number of moles of charged propylene, isobutylene or tertiary butanol}} \times 100$$

Selectivity (mol%) =

$$\frac{\text{Number of moles of produced acrolein and acrylic acid or methacrolein and methacrylic acid}}{\text{Number of moles of reacted propylene, isobutylene or tertiary butanol}} \times 100$$

Total yield of a single flow (mol%) =

$$\frac{\text{Number of moles of produced acrolein and acrylic acid or methacrolein and methacrylic acid}}{\text{Number of moles of charged propylene, isobutylene or tertiary butanol}} \times 100$$

#### [EXAMPLE I]

##### Preparation of suspension of catalyst material

While 4,500 ml of distilled water was heated with stirring, 3,186 g of ammonium molybdate and 972 g of ammonium paratungstate were added and dissolved therein. Separately, a solution of 2,100 g of cobalt nitrate in 400 ml of distilled water, a solution of 729 g of ferric nitrate in 600 ml of distilled water and a solution of 876 g of bismuth nitrate in 900 ml of distilled water acidified by addition of 180 ml of

concentrated nitric acid were prepared respectively, and a mixture of these three nitrate solutions was added to the above water solution containing ammonium molybdate and ammonium paratungstate. Then, a liquid obtained by dissolving 732 g of silica sol containing 20% by weight of silica and 6.06 g of potassium hydroxide in 450 ml of distilled water was added and stirred to prepare the suspension. (This suspension is referred to as suspension-A.)

#### EXAMPLE I-1 (Centrifugal flow coating method)

The suspension-A was heated, stirred, evaporated and dried to solidify it, and then the resulting solid was milled to about 100 mesh to obtain a powder. This powder was charged into a centrifugal flow coating device blowing heated air at 90°C with using distilled water as a binder, and formed into spherical particles having the average diameter of 5mm. These particles were dried in a drier at 120°C for 12 hours and then fired under an air current at 450°C for 6 hours to prepare a catalyst (I-1). The ratio of elements other than oxygen in this catalyst oxide was  $\text{Co}_4\text{Bi}_1\text{Fe}_6\text{W}_2\text{Mo}_{10}\text{Si}_{1.35}\text{K}_{0.06}$ .

#### EXAMPLES I-2-1 and I-2-2 (Tablet forming method)

A suspension-A was prepared in the same way as in the above, and the suspension-A was evaporated with stirring under heat to solidify it. Then the resulting solid in block state was dried in a drier under air current at 200°C for 12 hours. The dried block was milled to not more than 100 mesh. 2% by weight of a carbon powder was added to this milled powder and the resulting mixture was formed into tablets having a diameter of 5mm and height of 5mm. The tablets were fired under air current at 450°C for 6 hours to prepare a catalyst (I-2-1). Then, the same procedure was repeated to prepare a catalyst (I-2-2).

#### EXAMPLES I-3-1 and I-3-2 (Extrusion method)

A suspension-A was prepared in the same way as in the above, and the suspension-A was condensed until it was extrudable, and extruded to form extrudates having a diameter of 5mm and height of 5mm. The extrudates were dried at 120°C for 12 hours and fired under air current at 450°C for 6 hours to prepare a catalyst (I-3-1). Then, the same procedure was repeated to prepare a catalyst (I-3-2).

#### EXAMPLES I-4 (Marmerizer-forming method)

A suspension-A was prepared in the same way as in the above, and the suspension-A was treated with externally applied heat for condensation thereof to obtain a soil-like product, 40% by weight of which was dissipated when it was fired at 500°C (i.e., its solid content was 60% by weight). This product was extruded to form extrudates having a diameter of 6mm and lengths of 4 to 7mm, and then the extrudates were subjected to a marmerizer to form elliptic spheres having a breadth of 3mm and length of 5mm. The elliptic spheres were dried at 120°C for 12 hours and fired under air current at 450°C for 6 hours to prepare a catalyst (I-4-1).

#### EXAMPLES I-5 (Rolling particle-forming method)

A suspension-A was prepared in the same way as in the above, and the suspension-A was evaporated and dried with stirring under heat to solidify it. The resulting solid was milled to about 100 mesh to obtain a powder. This powder was formed into spherical particles having the average diameter of use of a rolling particle-forming machine and heated air at 80°C and distilled water as a binder. The particles were dried at 120°C for 12 hours and then fired under air current at 450°C for 6 hours to prepare a catalyst (I-5).

EXAMPLES I-6 (Pill-forming method)

A suspension-A was prepared in the same way as in the above, and the suspension-A was treated with externally applied heat for condensation thereof to obtain a soil-like product, 45% by weight of which was dissipated when it was fired at 500°C (i.e., its solid content was 55% by weight). This product was formed into shapes having the average diameter of 5mm by the use of a usual pill-forming machine. This resulting spherical product was dried at 120°C for 12 hours and then fired under air current at 450°C for 6 hours to obtain a catalyst (I-6).

REACTION TEST

Catalysts I-1 to I-6 obtained in the above EXAMPLES (1,500 ml each) were charged respectively to steel reaction tubes having an internal diameter of 25.4mm, and a mixture gas composed of 7% by volume of propylene, 12.6% by volume of oxygen, 10% by volume of water vapor and 70.4% by volume of nitrogen was introduced therein to carry out catalytic gas phase oxidation reactions of propylene at a reaction temperature of 310°C for a contact time of 2.25 seconds. The results are shown in Table 1.

[EXAMPLE II (Preparation of catalyst and its reproducibility)]

Catalyst material suspensions-A were prepared on a scale four times as large as that of EXAMPLES I-1 to I-6 series, and catalysts (EXAMPLES II-1 to II-4) were prepared by using the suspensions-A, by using forming methods shown in Table 2 and according to EXAMPLE I. In each of EXAMPLES II-1 to II-4, four catalysts were prepared under the same conditions (batch Nos. 1 to 4) in order to test the presence or absence of the reproducibility of catalyst preparation. Tests of performance were carried out according to the method of EXAMPLES I-1 to I-6. The results are shown in Table 2.

As is clear in Table 2, it is seen that the formation by a centrifugal flow coating method can give catalysts having smaller variation of physical values and high activity. The fact that the variation of physical values is small means that catalysts were prepared with good reproducibility. On the other hand, it is further seen that catalysts prepared by the other forming methods include those that have not the specific surface area, pore volume and pore diameter specified by the present invention although they were prepared in batches under entirely the same conditions, and that the catalyst performance thereof is inferior to that of the catalysts obtained by a centrifugal flow coating method.

[EXAMPLE III]Preparation of catalyst material suspension

The preparation of the catalyst material suspension for EXAMPLES I-1 to I-6 series was repeated except that thallium nitrate and barium nitrate were used in place of potassium hydroxide. The resulting suspension is referred to as suspension-B.

EXAMPLES III-1 (Centrifugal flow coating method)

The suspension-B was treated in the same way as in EXAMPLE I-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Co}_2\text{Bi}_2\text{Fe}_2\text{W}_2\text{Mo}_{10}\text{Si}_{1.35}\text{Ti}_{0.04}\text{Ba}_{0.05}$ .

EXAMPLES III-2-1 and II-2-2 (Tablet-forming method)

The suspension-B was treated according to the process described in EXAMPLE I-2 to prepare catalysts.

[EXAMPLE IV]

Preparation of catalyst material suspension

The preparation of the catalyst material suspension for EXAMPLES I-1 to I-6 series was repeated except that cesium nitrate was used in place of potassium hydroxide, and further, titanium dioxide was also used together with silica sol containing 20% by weight of silica. The resulting suspension is referred to as suspension-C.

EXAMPLE IV-1

The suspension-C was treated in the same way as in EXAMPLE I-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Co}_4\text{Bi}_1\text{Fe}_1\text{W}_2\text{Mo}_{10}\text{Si}_{1.35}\text{Cs}_{0.02}\text{Ti}_{1.0}$ .

EXAMPLES IV-2-1 and IV-2-2 (Extrusion method)

The suspension-C was treated according to EXAMPLE I-3 to prepare catalysts.

[EXAMPLES V]Preparation of catalyst material suspension

The preparation of the catalyst material suspension for EXAMPLES I-1 to I-6 series was repeated except that strontium nitrate was used in place of potassium hydroxide. The resulting suspension is referred to as suspension-D.

EXAMPLE V-1 (Centrifugal flow coating method)

The suspension-D was treated in the same way as in EXAMPLE I-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Co}_4\text{Bi}_1\text{Fe}_1\text{W}_2\text{Mo}_{10}\text{Si}_{1.35}\text{Sr}_{0.06}$ .

EXAMPLES V-2-1 and V-2-2 (Marmerizer-forming method)

The suspension-D was treated according to EXAMPLE I-4 to prepare catalysts.

[EXAMPLE VI]Preparation of catalyst material suspension

The preparation of the catalyst material suspension for EXAMPLES I-1 to I-6 series was repeated except that calcium nitrate was used in place of potassium hydroxide, and further, silica sol and calcium nitrate were added and then niobium pentoxide was added. The resulting suspension is referred to as suspension-E.

EXAMPLE VI-1 (Centrifugal flow coating method)

The suspension-E was treated in the same way as in EXAMPLE I-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Co}_4\text{Bi}_1\text{Fe}_1\text{W}_2\text{Mo}_{10}\text{Si}_{1.35}\text{Ca}_{0.06}\text{Nb}_{0.5}$ .

EXAMPLES VI-2-1 and VI-2-2 (Rolling particle-forming method)

The suspension-E was treated according to EXAMPLE I-5 to prepare catalysts.



## [EXAMPLE VII]

Preparation of catalyst material suspension

5 In preparing a catalyst material suspension in the same way as in the preparation of the catalyst suspension for EXAMPLES I-1 to I-6 series, nickel nitrate was added together with cobalt nitrate, rubidium nitrate was used in place of potassium hydroxide and phosphoric acid was used in place of ammonium paratungstate. The resulting suspension is referred to as suspension-F.

10

EXAMPLE VII-1 (Centrifugal flow coating method)

The suspension-F was treated in the same way as in EXAMPLE I-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Co}_3\text{Ni}_1\text{Bi}_1\text{Fe}_2\text{Mo}_{1.2}\text{Si}_{4.7}\text{P}_{1.0}\text{Rb}_{0.1}$

15

EXAMPLES VII-2-1 and VII-2-2 (Pill-forming method)

The suspension-F was treated according to EXAMPLE I-6 to prepare catalysts.

20

## [EXAMPLE VIII]

Preparation of catalyst material suspension

25

In preparing a catalyst material suspension in the same way as in the preparation of the catalyst suspension for EXAMPLES I-1 to I-6 series, nickel nitrate and aluminum nitrate were added together with cobalt nitrate and boric acid was used in place of ammonium paratungstate. The resulting suspension is referred to as suspension-G.

30

EXAMPLE VIII-1 (Centrifugal flow coating method)

35 The suspension-G was treated in the same way as in EXAMPLE I-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Co}_3\text{Ni}_1\text{Bi}_1\text{Fe}_2\text{Mo}_{1.2}\text{Si}_{4.7}\text{B}_{2.0}\text{K}_{0.2}\text{Al}_{1.0}$ .

EXAMPLES VIII-2-1 and VIII-2-2 (Tablet-forming method)

40

The suspension-G was treated according to EXAMPLE I-2 to prepare catalysts.

EXAMPLES VIII-3-1 and VIII-3-2 (Extrusion method)

45

The suspension-G was treated according to EXAMPLE I-3 to prepare catalysts.

## [EXAMPLE IX]

Preparation of catalyst material suspension

55 In preparing a catalyst material suspension in the same way as in the preparation of the catalyst suspension for EXAMPLES I-1 to I-6 series, nickel nitrate was added together with cobalt nitrate, potassium nitrate was used in place of potassium hydroxide and arsenious acid was used in place of ammonium paratungstate. The resulting suspension is referred to as suspension-H.

EXAMPLE IX-1 (Centrifugal flow coating method)

The suspension-H was treated in the same way as in EXAMPLE I-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Co}_2\text{Ni}_1\text{Bi}_1\text{Fe}_2\text{Mo}_{1.2}\text{Si}_{4.7}\text{As}_{0.5}\text{Ti}_{0.05}$ .

EXAMPLES IX-2-1 and IX-2-2 (Tablet-forming method)

The suspension-H was treated according to EXAMPLE I-2 to prepare catalysts.

EXAMPLES IX-3-1 and IX-3-2 (Extrusion method)

The suspension-H was treated according to EXAMPLE I-3 to prepare catalysts.

EXAMPLES IX-4-1 and IX-4-2 (Marmerizer-forming method)

The suspension-H was treated according to EXAMPLE I-4 to prepare catalysts.

EXAMPLES IX-5-1 and IX-5-2 (Rolling particle-forming method)

The suspension-H was treated according to EXAMPLE I-5 to prepare catalysts.

EXAMPLES IX-6-1 and IX-6-2 (Pill-forming method)

The suspension-H was treated according to EXAMPLE I-6 to prepare catalysts.

[EXAMPLE X]

The preparation of the suspension for EXAMPLES I-1 to I-6 series was repeated to prepare a suspension. This suspension is referred to as suspension I. The suspension-I was shaped, dried and fired in the same way as in EXAMPLE I-1 to prepare a catalyst. However, this EXAMPLE used 40% by weight aqueous solution of ammonium nitrate as a binder. Reaction test was carried out according to the method of EXAMPLES I-1 to I-6. The resulting catalyst had a specific surface area of  $12.3\text{m}^2/\text{g}$ , a pore volume of  $0.51\text{cc/g}$  and a pore volume distribution in which the pore volume consisting of pores having pore diameter in the range from 1 to 10  $\mu\text{m}$  was 55% and the pore volume consisting of pores having pore diameter in the range from 0.1 to 1(exclusive) $\mu\text{m}$  pores was 45%. This catalyst exhibited performance that the conversion of propylene was 99.2 mol%, the yield of acrolein in a single flow was 85.7 mol% and that the yield of acrylic acid in a single flow was 9.1 mol%.

Table 1

EXAMPLE	Forming method	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distribution		Reaction temperature (°C)	Conversion of propylene (mol%)	Yield in single flow (mol%)	
				*1 A	*2 B			Acrolein	Acrylic acid
Example I-1	Centrifugal flow coating method	10.6	0.460	35	62	310	98.7	85.4	9.5
Example I-2-1	Tablet-forming method	8.2	0.350	5	90	310	90.3	75.9	8.1
Example I-2-2	Tablet-forming method	4.2	0.250	0	92	310	86.5	69.2	10.1
Example I-3-1	Extrusion method	8.7	0.380	10	85	310	92.3	78.5	9.0
Example I-3-2	Extrusion method	3.5	0.230	0	97	310	90.0	75.1	9.8
Example I-4	Marmerizer-forming method	10.1	0.500	30	64	310	91.8	78.9	9.3
Example I-5	Rolling particle-forming method	12.5	0.400	35	60	310	93.0	77.1	10.9
Example I-6	Pill-forming method	9.5	0.380	35	59	310	93.4	77.6	10.0

\*1 Ratio(%) of pore volume consisting of pores having diameters in the range from 1 to 10  $\mu$ m to the entire pore volume

\*2 Ratio(%) of pore volume consisting of pores having diameters in the range from 0.1 to 1 (exclusive)  $\mu$ m to the entire pore volume

Table 2

EXAMPLE	Forming method	Batch No.	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distribution		Reaction temperature (°C)	Conversion of propylene (mol%)	Yield in single flow (mol%)	
					*1 A	*2 B			Acrolein	Acrylic acid
Example II-1	Centrifugal flow coating method	1	10.5	0.460	33	65	310	98.9	85.5	9.7
	"	2	10.1	0.480	35	61	310	98.1	85.7	9.3
	"	3	10.3	0.450	33	64	310	98.5	85.2	9.4
	"	4	10.7	0.460	32	65	310	99.2	85.0	10.5
Example II-2	Tablet-forming method	1	9.5	0.330	40	56	310	93.2	75.5	9.1
	"	2	4.0	0.250	15	75	310	88.7	73.7	8.4
	"	3	10.2	0.370	35	62	310	92.0	75.3	8.1
	"	4	7.4	0.350	43	53	310	90.6	76.0	9.1
Example II-3	Extrusion method	1	7.5	0.350	35	60	310	91.9	78.7	9.5
	"	2	5.0	0.270	45	47	310	87.1	76.2	7.0
	"	3	8.1	0.360	37	62	310	92.1	79.1	8.9
	"	4	6.7	0.320	41	43	310	89.6	78.5	8.1
Example II-4	Rolling particle-forming method	1	11.7	0.420	27	68	310	93.5	78.6	9.2
	"	2	10.1	0.450	18	72	310	90.5	77.9	8.5
	"	3	13.5	0.480	21	71	310	93.0	79.3	8.6
	"	4	8.6	0.360	35	57	310	89.1	77.4	8.6

\*1 &amp; \*2 Same as the remarks to Table 1.

Table 3

EXAMPLE	Forming method	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distribution		Reaction temperature (°C)	Conversion of propylene (mol%)	Yield in single flow (mol%)	
				*1 A	*2 B			Acrolein	Acrylic acid
III	III-1	12.5	0.410	32	60	310	99.5	87.8	7.2
	III-2-1	10.2	0.320	31	61	310	93.1	77.3	10.2
	III-2-2	7.8	0.230	45	46	310	87.9	74.2	9.3
IV	IV-1	9.2	0.430	45	50	310	91.0	82.3	6.0
	IV-2-1	8.5	0.350	29	63	310	88.5	75.2	6.3
	IV-2-2	6.9	0.180	0	92	310	85.1	68.9	7.3
V	V-1	10.5	0.430	35	59	310	98.3	88.9	6.1
	V-2-1	9.2	0.350	30	65	310	92.7	78.8	9.5
	V-2-2	8.7	0.270	32	61	310	90.3	77.1	8.9
VI	VI-1	11.2	0.420	38	60	310	98.7	87.8	6.0
	VI-2-1	10.2	0.350	33	61	310	94.3	81.0	7.0
	VI-2-2	7.8	0.280	27	65	310	90.2	79.0	7.3
VII	VII-1	10.7	0.380	34	58	310	95.6	81.0	9.6
	VII-2-1	10.2	0.300	37	57	310	91.3	75.8	8.4
	VII-2-2	7.9	0.260	41	50	310	88.5	73.5	8.7

-- to be continued --

\*1 &amp; \*2 Same as the remarks to Table 1.

Table 3 (continued)

EXAMPLE	Forming method	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distribution		Reaction temperature (°C)	Conversion of propylene (mol%)	Yield in single flow (mol%)	
				*1 A	*2 B			Acrolein	Acrylic acid
VIII	VIII-1 Centrifugal flow coating method	9.5	0.350	30	65	310	93.0	74.1	9.6
	VIII-2-1 Tablet-forming method	9.0	0.310	10	82	310	89.3	71.4	8.3
	VIII-2-2 Tablet-forming method	8.5	0.250	0	90	310	86.1	69.2	7.1
IX	IX-1 Centrifugal flow coating method	10.3	0.420	34	60	310	97.2	81.6	6.3
	IX-2-1 Tablet-forming method	9.7	0.320	30	59	310	90.1	75.7	6.1
	IX-2-2 Tablet-forming method	8.5	0.250	0	89	310	88.2	73.4	6.0
	IX-3-2 Extrusion method	9.0	0.370	27	68	310	93.1	76.1	7.1
	IX-3-2 Extrusion method	8.8	0.270	0	93	310	90.3	74.7	6.7
	IX-4-1 Marmerizer-forming method	9.2	0.360	35	60	310	93.2	76.9	7.1
	IX-4-2 Marmerizer-forming method	8.7	0.210	42	49	310	90.6	75.2	7.2
	IX-5-1 Rolling particle-forming method	11.2	0.420	41	55	310	94.1	77.6	7.5
	IX-5-2 Rolling particle-forming method	9.1	0.350	44	54	310	92.7	76.5	6.9
	IX-6-1 Pill-forming method	10.1	0.400	31	65	310	91.6	75.3	7.2
	IX-6-2 Pill-forming method	8.5	0.290	42	50	310	89.7	73.2	7.0

\*1 &amp; \*2 Same as the remarks to Table 1.

## [EXAMPLES XI]

Preparation of catalyst material suspension

Cobalt nitrate (14.56kg) and 2.02kg of ferric nitrate were dissolved in 10 liters of distilled water. 2.43 kg of bismuth nitrate was also dissolved in a nitric acid/distilled water solution consisting of 300ml of concentrated nitric acid and 1,200ml of distilled water. Separately, while 30 liters of distilled water was heated with stirring, 10.59kg of ammonium paramolybdate and 2.65kg of ammonium paratungstate were respectively added and dissolved therein, and the above two aqueous solutions of nitrate were added dropwise to the solution. And then an aqueous solution of 390g of cesium nitrate in 1 liter of distilled water and 2.03 kg of 20%-by-weight-concentrated silica sol were consecutively added thereto and dissolved to obtain a suspension. (The resulting suspension is referred to as suspension-J.)

EXAMPLE XI-1-1 (Centrifugal flow coating method)

A part of the suspension-J was evaporated and dried to solidify it while it was heated with stirring, and then the resulting solid in the state of block was dried in a drier at 200°C for 5 hours and milled to not more than 100 mesh to obtain a powder.

At first, alaph-alumina particles having the average diameter of 1mm were charged into a centrifugal flow coating device. And then the above powder was charged into the device blowing heated air at 90°C with using distilled water as a binder and formed into spherical particles having the average diameter of 5mm. The resulting spherical particles were fired under an air current at 500°C for 6 hours. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{12}\text{W}_2\text{Co}_{16}\text{Bi}_1\text{Fe}_1\text{Si}_{1.35}\text{Cs}_{0.4}$ .

EXAMPLE XI-1-2 (Centrigugal flow coating method)

EXAMPLE XI-1-1 was repeated except that 40% by weight aqueous solution of ammonium nitrate was used as a binder in place of distilled water, to prepare a catalyst.

EXAMPLES XI-2-1 and XI-2-2 (Tablet-forming method)

A part of the suspension-J was evaporated and dried with stirring under heat to produce a block state. The blocked product was dried in a drier under an air current at 200°C for 5 hours. This dried block was milled to not more than 100 mesh. 2% by weight of a carbon powder was added to the milled powder and the resulting mixture was formed into tablets having a diameter of 5mm and height of 5mm. The tablets were fired under an air current at 500°C for 6 hours to prepare a catalyst (XI-2-1). And then the same procedurê was repeated to prepare a catalyst (XI-2-2).

EXAMPLES XI-3-1 and XI-3-2 (Extrusion method)

A part of the suspension-J was evaporated and condensed until it was extrudable, and extruded to form extrudates having a diameter of 5mm and height of 5mm. The extrudates were fired under air current at 500°C for 6 hours to prepare a catalyst (XI-3-1). Then, the same procedure was repeated to prepare a catalyst (XI-3-2).

EXAMPLES XI-4 (Marmerizer-forming method)

A part of the suspension-J was treated with externally applied heat for condensation until it was extrudable. And the product was extruded to form extrudates having a diameter of 6mm and lengths of 4 to 7mm, and then the extrudates were subjected to a marmerizer to form elliptic spheres having a breadth of 3mm and length of 5mm. The elliptic spheres were fired under air current at 500°C for 6 hours to prepare a catalyst (XI-4).

10 EXAMPLES XI-5 (Rolling particle-forming method)

A part of the suspension-J was evaporated and dried with stirring under heat to solidify it into a block state. The resulting solid was dried in a drier at 200°C for 5 hours and milled to about 100 mesh to obtain a powder. At first, alpha-alumina having the average diameter of 1mm was charged into a rolling particle-forming machine and then the above powder was charged into the machine. By the use of heated air at 80°C and distilled water as a binder, the mixture was formed into spherical particles having the average diameter of 5mm. The particles were fired under an air current at 500°C for 6 hours to prepare a catalyst (XI-5).

20 EXAMPLES XI-6 (pill-forming method)

A part of the suspension-J was treated with externally applied heat for condensation thereof to obtain a soil-like product, 50% by weight of which was dissipated when it was fired at 500°C. This product was formed into shapes having the average diameter of 5mm by the use of a usual pill-forming machine. The resulting spherical product was fired under an air current at 500°C for 6 hours to obtain a catalyst (XI-6).

REACTION TEST

30 Catalysts XI-1 to XI-6 obtained in the above EXAMPLES (1,500 ml each) were changed respectively to steel reaction tubes having an internal diameter of 25.4mm, and a mixture gas composed of 6% by volume of isobutylene, 13.2% by volume of oxygen, 15% by volume of water vapor and 85.8% by volume of nitrogen was introduced thereinto to carry out reactions at reaction temperatures of 330 to 340°C and at a space velocity of 1,600hr<sup>-1</sup>. The results are shown in Table 4.

40

45

50

55



Table 4

Ex- ample	Forming method	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distrib- ution		Re- action temper- ature (°C)	Conver- sion of iso- butylene (mol%)	Selectivity		Total yield in single flow (mol%)
				*1 A	*2 B			Meth- acrolein	Meth- acrolein acid	
XI-1-1	Centrifugal flow coating method	3.0	0.420	58	39	330	99.3	85.1	3.4	87.9
XI-1-2	"	2.9	0.415	56	40	330	99.5	86.0	3.0	88.6
XI-2-1	Tablet-forming method	1.8	0.312	23	75	340	98.0	83.7	3.7	85.7
XI-2-2	"	2.1	0.300	20	78	340	97.5	84.2	3.2	85.2
XI-3-1	Extrusion method	2.2	0.350	35	63	340	98.6	84.0	3.5	86.3
XI-3-2	"	2.0	0.372	31	66	340	98.1	84.4	3.0	85.7
XI-4	Marmerizer-forming method	2.1	0.342	37	61	340	98.7	84.1	3.4	86.4
XI-5	Rolling particle- forming method	2.7	0.372	42	55	340	98.2	84.7	2.2	85.3
XI-6	Pill-forming method	2.6	0.321	35	63	340	97.8	84.1	2.7	84.9

\*1 Ratio(%) of pore volume consisting of pores having diameters in the range from 1 to 10  $\mu$ m to the entire pore volume

\*2 Ratio(%) of pore volume consisting of pores having diameters in the range from 0.1 to 1 (exclusive)  $\mu$ m to the entire pore volume

[EXAMPLE XII (Preparation of catalyst and its reproducibility)]

5 A suspension-J was prepared in the same way as in EXAMPLE XI, and catalysts (EXAMPLES XII-1 to XII-6) were prepared by the use of the suspension-J and six different forming methods shown in Table 5 according to EXAMPLE XI. In each of EXAMPLES XII-1 to XII-6, four catalysts were prepared under the same conditions (batch Nos. 1 to 4) in order to test the presence or absence of the reproducibility of catalyst preparation. Tests of performance were carried out according to the method of EXAMPLES XI-1 to XI-6 series. With regard to EXAMPLE XII-1, the method of EXAMPLE XI-1-1 was applied. The results are shown in Table 5.

10 As is clear in Table 5, it is seen that the formation by a centrifugal flow coating method can give catalysts having smaller variation of physical values and high activity. The fact that the variation of physical values is small means that catalysts were prepared with good reproducibility. On the other hand, it is further seen that catalysts prepared by the other forming methods include those that have not physical values specified by the present invention although they were prepared in batches under entirely the same conditions, and that the catalyst performance thereof is inferior to that of the catalysts obtained by a centrifugal flow coating method.

Table 5

Ex- ample	Forming method	Batch No.	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distribution		Re- action temper- ature (°C)	Conver- sion of iso- butylene (mol%)	Selectivity		Total yield in single flow (mol%)
					*1 A	*2 B			Meth- acrolein	Meth- acrolein acid	
XII-1	Centrifugal flow coating method	1	2.9	0.417	58	40	330	99.2	85.3	3.6	88.2
		2	3.0	0.420	59	40	330	99.0	85.2	3.5	87.8
		3	2.9	0.418	60	38	330	99.4	85.6	3.2	88.2
		4	3.1	0.420	59	40	330	99.3	85.3	3.5	88.2
XII-2	Tablet-forming method	1	1.7	0.312	20	77	340	98.1	83.6	3.5	85.4
		2	1.5	0.297	19	80	340	97.6	83.1	3.5	84.5
		3	1.1	0.253	24	75	340	97.2	83.7	3.6	84.9
		4	2.0	0.330	18	80	340	98.2	82.2	3.2	85.8
XII-3	Extrusion method	1	2.4	0.380	35	63	340	98.9	84.1	3.3	86.4
		2	2.1	0.292	31	66	340	98.1	82.7	3.4	84.5
		3	1.8	0.270	38	59	340	97.6	83.6	3.3	84.8
		4	2.2	0.350	30	66	340	98.5	82.1	3.2	84.0
XII-4	Marmerizer-forming method	1	2.5	0.301	35	64	340	98.1	82.7	3.4	84.5
		2	2.0	0.295	28	71	340	97.2	82.5	3.4	83.5
		3	2.2	0.300	30	68	340	97.8	83.5	3.2	84.8
		4	2.6	0.312	37	61	340	98.3	82.1	3.4	84.0

\*1 &amp; \*2 Same as the remarks to Table 4

- to be continued -

Table 5 (continued)

Ex-ample	Forming method	Batch No.	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distribution		Re-action temperature (°C)	Conver-sion of iso-butylene (mol%)	Selectivity		Total yield in single flow (mol%)
					*1 A	*2 B			Meth-acrolein	Meth-acrolein acid	
XII-5	Rolling particle-forming method	1	2.5	0.365	41	58	340	98.2	84.1	3.5	86.0
		2	2.9	0.400	34	64	340	98.7	83.5	3.4	85.8
		3	2.1	0.312	31	68	340	97.5	83.2	3.3	84.3
		4	2.6	0.354	40	57	340	98.1	83.6	3.4	85.3
XII-6	Pill-forming method	1	2.1	0.312	28	71	340	97.6	82.7	3.3	83.9
		2	2.4	0.341	31	68	340	97.1	83.6	3.3	84.4
		3	2.9	0.378	34	64	340	98.1	83.1	3.3	84.8
		4	2.7	0.350	39	60	340	96.5	84.2	3.3	84.5

\*1 &amp; \*2 Same as the remarks to Table 4

## [EXAMPLE XVIII]

5

Preparation of catalyst material suspension

EXAMPLE XI was repeated except that 230.9g of rubidium nitrate and 50.5g of potassium nitrate were used in place of cesium nitrate to obtain a suspension (the resulting suspension is referred to as suspension-K).

10

EXAMPLE XIII-1 (Centrifugal flow coating method)

15

A part of the suspension-K was treated in the same way as in EXAMPLE XI-1-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{0.2}\text{W}_2\text{Co}_7\text{Bi}_3\text{Fe}_1\text{Si}_{1.35}\text{Rb}_{0.4}\text{K}_{0.1}$ .

EXAMPLES XIII-2-1 and XIII-2-2 (Tablet-forming method)

20

A part of the suspension-K was treated in the same way as in EXAMPLE XI-2 to prepare a catalyst.

REACTION TEST

25

By the use of the catalysts obtained in EXAMPLES XIII-1 and XIII-2, reactions were carried out in the same way as in EXAMPLE XI. The results are shown in Table 6.

## 30 [EXAMPLE XIV]

Preparation of catalyst material suspension

35

EXAMPLE XIII was repeated except that 21.0g of lithium hydroxide and 127.5g of sodium nitrate were used in place of cesium nitrate and potassium nitrate to obtain a suspension (which is referred to as suspension-L).

EXAMPLE XIV-1 (Centrifugal flow coating method)

40

A part of the suspension-L was treated in the same way as in EXAMPLE XI-1-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{0.2}\text{W}_2\text{Co}_7\text{Bi}_3\text{Fe}_1\text{Si}_{1.35}\text{Li}_{0.1}\text{Na}_{0.3}$ .

45 EXAMPLES XIV-2-1 and XIV-2-2 (Extrusion method)

A part of the suspension-K was treated in the same way as in EXAMPLE XI-3 to prepare a catalyst.

50 REACTION TEST

By the use of the catalysts obtained in EXAMPLES XIV-1 and XIV-2, reactions were carried out in the same way as in EXAMPLE XI. The results are shown in Table 6.

55

## [EXAMPLE XV]

Preparation of catalyst material suspension

EXAMPLE XI was repeated except that 115.3g of 85% orthophosphoric acid was added after ammonium paratungstate and that 532.7g of thallium nitrate was used in place of cesium nitrate, to obtain a suspension (which is referred to as suspension-M).

EXAMPLE XV-1 (Centrifugal flow coating method)

A part of the suspension-M was treated in the same way as in EXAMPLE XI-1-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{1.2}\text{W}_2\text{Co}_{1.6}\text{Bi}_1\text{Fe}_1\text{Si}_{1.35}\text{Tl}_{0.4}\text{P}_{0.2}$ .

EXAMPLES XV-2-1 and XV-2-2 (Marmerizer-forming method)

A part of the suspension-M was treated in the same way as in EXAMPLE XI-4 to prepare a catalyst.

REACTION TEST

By the use of the catalysts obtained in EXAMPLES XV-1 and XV-2, reactions were carried out in the same way as in EXAMPLE XI. The results are shown in Table 6.

[EXAMPLE XVI]

Preparation of catalyst material suspension

EXAMPLE XI was repeated except that 11.6 kg of nickel nitrate was used in place of cobalt nitrate and that 1,282g of magnesium nitrate and 1,180.7g of calcium nitrate were used together with 195g of cesium nitrate, to obtain a suspension (which is referred to as suspension-N).

EXAMPLE XVI-1 (Centrifugal flow coating method)

A part of the suspension-N was treated in the same way as in EXAMPLE XI-1-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{1.2}\text{W}_2\text{Ni}_1\text{Bi}_1\text{Fe}_1\text{Si}_{1.35}\text{Cs}_{0.2}\text{Mg}_{1.0}\text{Ca}_{1.0}$ .

EXAMPLES XVI-2-1 and XVI-2-2 (Rolling particle-forming method)

A part of the suspension-N was treated in the same way as in EXAMPLE XI-5 to prepare a catalyst.

REACTION TEST

By the use of the catalysts obtained in EXAMPLES XVI-1 and XVI-2, reactions were carried out in the same way as in EXAMPLE XI. The results are shown in Table 6.

[EXAMPLE XVII]

Preparation of catalyst material suspension

EXAMPLE XI was repeated except that 1,306.7g of barium nitrate and 1,058.1g of strontium nitrate were used in place of magnesium nitrate and calcium nitrate to obtain a suspension (which is referred to as suspension-O).

EXAMPLE XVII-1 (Centrifugal flow coating method)

A part of the suspension-0 was treated in the same way as in EXAMPLE XI-1-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{1.2}\text{W}_2\text{Ni}_8\text{Bi}_1\text{Fe}_1\text{Si}_{1.35}\text{Cs}_{0.2}\text{Ba}_{1.0}\text{Sr}_{1.0}$ .

EXAMPLES XVII-2-1 and XVII-2-2 (Pill-forming method)

A part of the suspension-0 was treated in the same way as in EXAMPLE XI-6 to prepare a catalyst.

REACTION TEST

By the use of the catalysts obtained in EXAMPLES XVII-1 and XVII-2, reactions were carried out in the same way as in EXAMPLE XI. The results are shown in Table 6.

[EXAMPLE XVIII]Preparation of catalyst material suspension

In preparing a catalyst material suspension in the same way as in EXAMPLE XI, ammonium paratungstate was not used, the amount of ferric nitrate used was changed to 6.06kg, the amount of cobalt nitrate used was changed to 10.2kg, the amount of cesium nitrate used was changed to 97.5g, the amount of 20%-by-weight-concentrated silica sol used was changed to 16.5kg and 1,656g of lead nitrate was added before the above silica sol, which gave a suspension. (The suspension is referred to as suspension-P.)

EXAMPLE XVIII-1 (Centrifugal flow coating method)

A part of the suspension-P was treated in the same way as in EXAMPLE XI-1-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{1.2}\text{Co}_7\text{Bi}_1\text{Fe}_3\text{Si}_{1.1}\text{Cs}_{0.1}\text{Pb}_{1.0}$ .

EXAMPLES XVIII-2-1 and XVIII-2-2 (Tablet-forming method)

A part of the suspension-P was treated in the same way as in EXAMPLE XI-2 to prepare a catalyst.

REACTION TEST

By the use of the catalyst obtained in EXAMPLES XVIII-1 and XVIII-2, reactions were carried out in the same way as in EXAMPLE XI. The results are shown in Table 6.

[EXAMPLE XIX]Preparation of catalyst material suspension

In preparing a catalyst material suspension in the same way as in EXAMPLE XI, ammonium paratungstate and cesium nitrate were not used, the amount of ferric nitrate used was changed to 6.06kg, 8.7kg of nickel nitrate and 399g of titanium dioxide were used respectively in place of cobalt nitrate and silica sol, 2.9kg of antimony trioxide was added together with ammonium paramolybdate, and 753.4g of stannic oxide and 399.0g of tellurium dioxide were added before titanium dioxide, which gave a suspension. (The suspension is referred to as suspension-Q.)

EXAMPLE XIX-1 (Centrifugal flow coating method)

A part of the suspension-Q was treated in the same way as in EXAMPLE XI-1-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{1.2}\text{Ni}_4\text{Bi}_4\text{Fe}_3\text{Ti}_1\text{Sb}_{2.0}\text{Sn}_1\text{Te}_{0.5}$ .

EXAMPLES XIX-2-1 and XIX-2-2 (Extrusion method)

A part of the suspension-P was treated in the same way as in EXAMPLE XI-3 to prepare a catalyst.

REACTION TEST

By the use of the catalysts obtained in EXAMPLES XIX-1 and XIX-2, reactions were carried out in the same way as in EXAMPLE XI. The results are shown in Table 6.

[EXAMPLE XX]Preparation of catalyst material suspension

In preparing a catalyst material suspension in the same way as in EXAMPLE XI, ammonium paratungstate was not used, the amount of cobalt nitrate used was changed to 7.3kg, the amount of ferric nitrate used was changed to 24.2kg, 252.7g of potassium nitrate was used in place of cesium nitrate and 1,875.6g of aluminum nitrate was used in place of silica sol, which gave a suspension. (The suspension is referred to as suspension-R.)

EXAMPLE XX-1 (Centrifugal flow coating method)

A part of the suspension-R was treated in the same way as in EXAMPLE XI-1-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{1.2}\text{Co}_5\text{Bi}_4\text{Fe}_{1.2}\text{Al}_{1.0}\text{K}_{0.5}$ .

EXAMPLES XX-2-1 and XX-2-2 (Marmerizer-forming method)

A part of the suspension-R was treated in the same way as in EXAMPLE XI-4 to prepare a catalyst.

REACTION TEST

By the use of the catalysts obtained in EXAMPLES XX-1 and XX-2, reactions were carried out in the same way as in EXAMPLE XI. The results are shown in Table 6.

[EXAMPLE XXI]Preparation of catalyst material suspension

In preparing a catalyst material suspension in the same way as in EXAMPLE XI, ammonium paratungstate was not used, 1,336.3g of zirconyl nitrate was used in place of silica sol, the amount of cobalt nitrate used was changed to 8.7kg and 1,435.2g of manganese nitrate, 1,487.4g of zinc nitrate and 664.5g of niobium pentaoxide were used at the last step, which gave a suspension. (The suspension is referred to as suspension-S.)



EXAMPLE XXI-1 (Centrifugal flow coating method)

A part of the suspension-S was treated in the same way as in EXAMPLE XI-1-1 to prepare a catalyst. The ratio of elements other than oxygen in this catalyst oxide was  $\text{Mo}_{1.2}\text{Co}_4\text{Bi.Fe.Zr.Cs}_{0.4}\text{Ce.Mn.Zn.Nb}_{0.5}$ .

EXAMPLES XXI-2-1 and XXI-2-2 (Rolling particle-forming method)

A part of the suspension-S was treated in the same way as in EXAMPLE XI-5 to prepare a catalyst.

REACTION TEST

By the use of the catalysts obtained in EXAMPLES XXI-1 and XXI-2, reactions were carried out in the same way as in EXAMPLE XI. The results are shown in Table 6.

Table 6

Example	Forming method	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distribution		Reaction temperature (°C)	Conversion of isobutylene (mol%)	Selectivity (mol%)		Total yield in single flow (mol%)
				*1 A	*2 B			Methacrolein	Methacrolein acid	
XIII	XIII-1	3.5	0.453	59	38	330	98.8	85.7	4.0	88.6
	XIII-2-2	2.1	0.334	28	71	340	95.1	83.1	4.4	83.2
	XIII-2-2	2.6	0.342	23	76	340	97.7	82.6	4.2	84.8
XIV	XIV-1	3.7	0.400	57	42	330	97.9	80.6	3.5	82.3
	XIV-2-1	2.7	0.351	36	62	340	97.1	78.0	4.5	80.1
	XIV-2-2	2.5	0.312	31	68	340	96.3	76.2	4.1	77.3
XV	XV-1	2.6	0.376	53	45	330	95.0	86.0	2.2	83.8
	XV-2-1	2.6	0.312	32	67	340	94.7	84.1	2.1	81.6
	XV-2-2	2.5	0.307	30	69	340	94.0	84.0	1.9	80.7

\*1 &amp; \*2 Same as the remarks to Table 4

- to be continued -

Table 6 (continued)

Example	Forming method	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distribution		Reaction temperature (°C)	Conversion of isobutylene (mol%)	Selectivity (mol%)		Total yield in single flow (mol%)
				*1 A	*2 B			Methacrolein	Methacrolein acid	
XVI	XVI-1	3.0	0.357	56	42	330	98.9	81.2	3.5	83.8
	XVI-2-1	3.0	0.314	42	56	340	98.0	79.5	3.2	81.0
	XVI-2-2	2.6	0.287	37	61	340	97.2	79.2	3.1	80.0
XVII	XVII-1	3.4	0.326	62	37	330	98.1	79.3	3.5	80.5
	XVII-2-1	2.5	0.302	41	56	340	96.2	78.1	4.1	79.1
	XVII-2-2	2.4	0.298	32	66	340	97.0	77.5	4.2	79.2
XVIII	XVIII-1	3.2	0.321	63	35	330	93.5	78.9	3.0	76.6
	XVIII-2-1	1.6	0.301	21	78	340	91.0	77.1	2.5	72.4
	XVIII-2-2	1.4	0.278	28	71	340	89.2	78.2	2.4	71.9

- to be continued -

\*1 &amp; \*2 Same as the remarks to Table 4

Table 6 (continued)

Example	Forming method	Specific surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter distribution		Reaction temperature (°C)	Conversion of isobutylene (mol%)	Selectivity (mol%)		Total yield in single flow (mol%)
				*1 A	*2 B			Methacrolein	Methacrolein acid	
XIX	XIX-1	3.3	0.376	62	36	330	89.6	78.1	3.0	72.7
	XIX-2-1	2.6	0.342	41	57	340	89.1	76.0	2.5	69.9
	XIX-2-2	2.5	0.310	29	69	340	88.0	75.1	3.0	68.7
XX	XX-1	2.9	0.362	57	42	330	94.8	76.0	4.0	75.8
	XX-2-1	2.8	0.314	35	62	340	94.1	71.9	5.0	72.4
	XX-2-2	2.4	0.276	27	70	340	93.6	70.3	5.5	70.9
XXI	XXI-1	3.8	0.396	64	35	330	93.2	74.0	6.0	74.6
	XXI-2-1	3.5	0.351	42	56	340	92.7	71.2	6.2	71.7
	XXI-2-2	3.2	0.306	36	61	340	92.0	69.5	6.1	69.6

\*1 &amp; \*2 Same as the remarks to Table 4

## [EXAMPLES XXII]

5

A reaction was carried out by the use of the catalyst obtained in batch No. 1 of EXAMPLE XII-1 and tertiary butanol in place of isobutylene. In the reaction test, EXAMPLE XII was repeated except that 6% by volume of tertiary butanol was used in place of isobutylene. (Accordingly, the gas after a dehydration reaction of tertiary butanol was composed, on an average, of 5.66% by volume of isobutylene, 12.45% by volume of oxygen, 19.81% by volume of water vapor and 62.08% by volume of nitrogen. And the space velocity was  $1,700\text{hr}^{-1}$ .) The results of the reaction were that the conversion ratio of tertiary butanol was 100 mole%, the selectivity to methacrolein was 84.9%, the selectivity to metacrylic acid was 3.4% and unreacted isobutylene was 1.3%. Based on this reaction, it is seen that the same result is obtained even if isobutylene is changed to tertiary butanol.

15

## [EXAMPLE XXIII]

By the use of the catalyst obtained in batch No. 2 of EXAMPLE XII-1, the reaction test for a long period of time of 8,000 hours was carried out. Said reaction test was carried out in the same way as in EXAMPLE XII. The temperature at the beginning of the reaction was  $330^{\circ}\text{C}$  and it was sufficient to raise the reaction temperature by only  $10^{\circ}\text{C}$  during the period of 8,000 hours. The results of the reaction at the time after 8,000 hours were that the conversion of isobutylene was 98.7 mol%, the selectivity to methacrolein was 85.3 mol% and the selectivity to methacrylic acid was 3.2 mol%.

25

## Claims

1. A catalyst used for producing, by catalytic gas phase oxidation of a  $\text{C}_3\text{-C}_5$  olefin or tertiary alcohol, the corresponding unsaturated aldehyde and unsaturated carboxylic acid, said catalyst characterized by comprising molybdenum, iron and bismuth and having a specific surface area in the range from 1 to  $20\text{m}^2/\text{gr}$ , a pore volume in the range from 0.1 to  $1.0\text{cc}/\text{gr}$  and a pore diameter distribution in which the pore diameters are collectively distributed in the range of each of from 1 to 10 microns and from 0.1 to 1 (exclusive) micron.

2. A process for preparing a catalyst comprising molybdenum, iron and bismuth and used for producing, by catalytic gas phase oxidation of a  $\text{C}_3\text{-C}_5$  olefin or tertiary alcohol, the corresponding unsaturated aldehyde and unsaturated carboxylic acid, said process comprising charging an unfired material powder into a centrifugal flow coating device to form particles having the average diameter of 2 to  $10\text{mm}$  and then firing the particles thereby to obtain, with good reproducibility, the catalyst which has a specific surface area in the range from 1 to  $20\text{m}^2/\text{gr}$ , a pore volume in the range from 0.1 to  $1.0\text{cc}/\text{gr}$  and a pore diameter distribution in which the pore diameters are collectively distributed in the range of each of from 1 to 10 microns and from 0.1 to 1 (exclusive) micron.

3. A catalyst for the oxidation of a  $\text{C}_3\text{-C}_5$  olefin according to claim 1 characterized by comprising molybdenum, iron and bismuth and having a specific surface area in the range from 5 to  $20\text{m}^2/\text{gr}$ , a pore volume in the range from 0.3 to  $0.9\text{cc}/\text{gr}$  and a pore diameter distribution in which the pore diameters are collectively distributed in the range of each of from 1 to 10 microns and from 0.1 to 1 (exclusive) micron.

4. A process for preparing a catalyst comprising molybdenum, iron and bismuth for the oxidation of propylene according to claim 2 characterized by charging an unfired material powder into a centrifugal flow coating device to form particles having the average diameter of 2 to  $10\text{mm}$  and then firing the particles thereby to obtain the catalyst which has a specific surface area in the range from 5 to  $20\text{m}^2/\text{gr}$ , a pore volume in the range from 0.3 to  $0.9\text{cc}/\text{gr}$  and a pore diameter distribution in which the pore diameters are collectively distributed in the range of each of from 1 to 10 microns and from 0.1 to 1 (exclusive) micron.

5. A catalyst for the oxidation of isobutylene or tertiary butanol according to claim 1 characterized by comprising molybdenum, iron and bismuth and having a specific surface area in the range from 1 to  $20\text{m}^2/\text{gr}$ , a pore volume in the range from 0.1 to  $1.0\text{cc}/\text{gr}$  and a pore diameter distribution in which the pore diameters are collectively distributed in the range of each of from 1 to 10 microns and from 0.1 to 1 (exclusive) micron.

6. A process for preparing a catalyst comprising molybdenum, iron and bismuth for the oxidation of isobutylene or tertiary butanol according to claim 2 characterized by charging an unfired material powder into a centrifugal flow coating device to form particles having the average diameter of 2 to 10mm and then firing the particles thereby to obtain the catalyst which has a specific surface area in the range from 1 to 20m<sup>2</sup>/gr, a pore volume in the range from 0.1 to 1.0cc/gr and a pore diameter distribution in which the pore diameters are collectively distributed in the range of each of from 1 to 10 microns and from 0.1 to 1 (exclusive) micron.

10

15

20

25

30

35

40

45

50

55



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 068 193 (DEGUSSA) ---		B 01 J 23/88
A	US-A-4 548 709 (BOWES) ---		C 07 C 51/25
A	FR-A-2 354 812 (BASF) ---		C 07 C 57/04
A	US-A-4 276 196 (DALTON) ---		C 07 C 45/32
A	EP-A-0 000 663 (STANDARD OIL CO.) ---		B 01 J 35/10
D,A	CHEMICAL ABSTRACTS, vol. 88, no. 12, 20th March 1978, page 373, abstract no. 79851b, Columbus, Ohio, US; & JP-A-77 117 292 (TAKEDA CHEMICAL INDUSTRIES, LTD) 01-10-1977 -----		B 01 J 37/02
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			B 01 J C 07 C
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	22-04-1988	LO CONTE C.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	